$\boxed{\text{問題4}}$

I. (1) $dG(T,H) = dU - SdT - TdS - MdH - HdM$
$= \cancel{TdS} + \cancel{HdM} - SdT - \cancel{TdS} - MdH - \cancel{HdM}$
$= -SdT - MdH$ //

(2) $dG(T,H) = \left(\frac{\partial G}{\partial T}\right)_H dT + \left(\frac{\partial G}{\partial H}\right)_T dH$ より

$$\begin{cases} \left(\frac{\partial G}{\partial T}\right)_H = -S \\ \left(\frac{\partial G}{\partial H}\right)_T = -M \end{cases} \quad \text{なので} \quad \begin{aligned} \frac{\partial^2 G}{\partial T \partial H} &= -\left(\frac{\partial S}{\partial H}\right)_T \\ \frac{\partial^2 G}{\partial H \partial T} &= -\left(\frac{\partial M}{\partial T}\right)_H \end{aligned}$$

よって、
$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \quad //$$

(3) 熱力学第1法則より $dU = d'Q + d'W$ がいえる。
また、熱容量 C は $C = \frac{d'Q}{dT}$ で定義される。

(i) 磁化一定のとき。

$$\begin{aligned} d'Q &= dU(T,M) - HdM \\ &= \left(\frac{\partial U}{\partial T}\right)_M dT + \left(\frac{\partial U}{\partial M}\right)_T dM - HdM \\ &= \left(\frac{\partial U}{\partial T}\right)_M dT + \left\{\left(\frac{\partial U}{\partial M}\right)_T - H\right\} dM \end{aligned}$$

$$C_M = \left(\frac{d'Q}{dT}\right)_M = \left(\frac{\partial U}{\partial T}\right)_M$$

(ii) 磁場一定のとき。

$$\begin{aligned} d'Q &= dU(T,H) - HdM \\ &= \left(\frac{\partial U}{\partial T}\right)_H dT + \left(\frac{\partial U}{\partial H}\right)_T dH - HdM(T,H) \\ &= \left(\frac{\partial U}{\partial T}\right)_H dT + \left(\frac{\partial U}{\partial H}\right)_T dH - H\cdot\left\{\left(\frac{\partial M}{\partial T}\right)_H dT + \left(\frac{\partial M}{\partial H}\right)_T dH\right\} \end{aligned}$$

$$\begin{aligned} C_H = \left(\frac{d'Q}{dT}\right)_H &= \left(\frac{\partial U}{\partial T}\right)_H - H\left(\frac{\partial M}{\partial T}\right)_H \\ &= \left(\frac{\partial U}{\partial T}\right)_H - H\alpha \quad // \end{aligned}$$

(4) 式☆より

$$dU = TdS + HdM$$

$$= T\left\{ \left(\frac{\partial S}{\partial T}\right)_H dT + \left(\frac{\partial S}{\partial H}\right)_T dH \right\} + H\left\{ \left(\frac{\partial M}{\partial T}\right)_H dT + \left(\frac{\partial M}{\partial H}\right)_T dH \right\}$$

$$= \left\{ T\left(\frac{\partial S}{\partial T}\right)_H + H\left(\frac{\partial M}{\partial T}\right)_H \right\} dT + \left\{ T\left(\frac{\partial S}{\partial H}\right)_T + H\left(\frac{\partial M}{\partial H}\right)_T \right\} dH$$

$$= (C_H + H\alpha)\, dT + (T\alpha + H\chi)\, dH$$

また、

$$dU(T, H) = \left(\frac{\partial U}{\partial T}\right)_H dT + \left(\frac{\partial U}{\partial H}\right)_T dH$$

であるから。 $\left(\frac{\partial U}{\partial H}\right)_T = T\alpha + H\chi$ //

(5) $dU(T, H(T, M)) = \left(\frac{\partial U}{\partial T}\right)_H dT + \left(\frac{\partial U}{\partial H}\right)_T dH$ 　　　また。

$$= \left(\frac{\partial U}{\partial T}\right)_H dT + \left(\frac{\partial U}{\partial H}\right)_T \left\{ \underbrace{\left(\frac{\partial H}{\partial T}\right)_M}_{= -\frac{\alpha}{\chi}} dT + \left(\frac{\partial H}{\partial M}\right)_T dM \right\}$$

$$= \left\{ C_H + H\alpha - (T\alpha + H\chi)\cdot\frac{\alpha}{\chi} \right\} dT + (T\alpha + H\chi)\cdot\left(\frac{\partial H}{\partial M}\right)_T dM.$$

また。

$$dU(T, M) = \left(\frac{\partial U}{\partial T}\right)_M dT + \left(\frac{\partial U}{\partial M}\right)_T dM$$

$$\therefore \left(\frac{\partial U}{\partial T}\right)_M = C_H + \cancel{H\alpha} - \frac{T\alpha^2}{\chi} - \cancel{H\alpha} = C_H - \frac{T\alpha^2}{\chi} \;//$$

II

(6) 磁場一様であるとき $h_i = h$ より 分配関数 Z は

$$Z = \sum_{\sigma_1=\pm1} \cdots \sum_{\sigma_N=\pm1} \exp(-\beta \mathcal{H})$$

$$= \sum_{\sigma_1=\pm1} \cdots \sum_{\sigma_N=\pm1} \prod_{i=1}^{N} \exp(+\beta\mu\sigma_i h)$$

$$= \prod_{i=1}^{N} \sum_{\sigma_i=\pm1} \exp(\beta\mu\sigma_i h)$$

$$= \prod_{i=1}^{N} \left(e^{\beta\mu h} + e^{-\beta\mu h} \right) = \left(e^{\beta\mu h} + e^{-\beta\mu h} \right)^N = (2\cosh\beta\mu h)^N \quad //$$

エネルギー期待値Eは、

$$E = \frac{\sum_\alpha H_\alpha e^{-\beta H_\alpha}}{\sum_\alpha e^{-\beta H_\alpha}}$$

※ 全部の状態ということで α とおいた。上でおいた i とは意味が違う。

$$= \frac{1}{Z} \sum_\alpha H_\alpha e^{-\beta H_\alpha}$$

$$= \frac{1}{Z} \sum_\alpha - \frac{\partial e^{-\beta H_\alpha}}{\partial \beta}$$

$$= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \log Z}{\partial \beta}$$

よって.

$$E = -N \frac{\partial \log 2\cosh\beta\mu h}{\partial \beta}$$

$$= -N \cdot \frac{\cancel{2}\sinh\beta\mu h}{\cancel{2}\cosh\beta\mu h} \cdot \mu h$$

$$= -N\mu h \tanh\beta\mu h \quad //$$

(7) それぞれの粒子は独立であり、相互作用していないので

$$Z = \prod_{i=1}^{N} Z_i$$

$$E = -\frac{\partial}{\partial\beta}\log Z = -\frac{\partial}{\partial\beta}\left(\sum_{i=1}^{N}\log Z_i\right) = \sum_{i=1}^{N} E_i$$

と書けるはずである。1粒子の分配関数 Z_i は.

$$Z_i = e^{-\beta\mu h\varepsilon_i} + e^{\beta\mu h\varepsilon_i}$$

$$\therefore \quad E_i = -\mu h\varepsilon_i \tanh\beta\mu h\varepsilon_i$$

$$\therefore \quad E = \sum_{i=1}^{N} E_i$$

$$= \int_0^{\varepsilon_{max}} d\varepsilon \cdot (-\mu h\varepsilon \tanh\beta\mu h\varepsilon) \cdot g(\varepsilon)$$

$$= -\int_0^{\varepsilon_{max}} d\varepsilon\ \mu h\varepsilon \tanh \beta\mu h\varepsilon\ \ g(\varepsilon)$$ //

(8) $$E = -\int_0^{\varepsilon_{Max}} d\varepsilon\ \mu h\varepsilon \tanh(\beta\mu h\varepsilon) \cdot NA\varepsilon^{r}$$

$$C = \frac{dE}{dT}$$

$$= k\beta^2 \int_0^{\varepsilon_{Max}} d\varepsilon\ NA\mu h\varepsilon^{r+1} \frac{d}{d\beta} \tan(\beta\mu h\varepsilon)$$

$$= \int_0^{\varepsilon_{Max}} d\varepsilon\ NA\mu^2 h^2 \varepsilon^{r+2} k\beta^2 \frac{1}{\cosh^2(\beta\mu h\varepsilon)}$$

(9) $r=0$、$\beta\mu\varepsilon_{max}h \sim \infty$ とする。
また、$x = \beta\mu\varepsilon h$ と変数変換すると、

$dx = \beta\mu h\, d\varepsilon$ より

$$C = \frac{ANk}{\beta\mu h} \underbrace{\int_0^{\infty} dx \frac{x^2}{\cosh^2 x}}_{=\frac{\pi^2}{12}}$$

$$= \frac{\pi^2}{12} \frac{kNA}{\beta\mu h} \propto T$$